



LARGE PLATE CdTe SYNTHESIS BY SEALED

VESSEL TRANSPORT

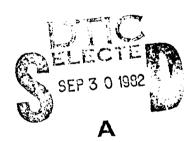
A. R. HILTON, PRINCIPAL INVESTIGATOR (214) 494-5624

QUARTERLY TECHNICAL REPORT NO. 3

REPORT PERIOD: JULY 1 - AUGUST 31, 1982

SEPTEMBER 1982

SPONSORED BY:



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AMORPHOUS MATERIALS, INC.

3130 BENTON • GARLAND, TEXAS 75042

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SUMMARY

The goal of this program is to use vapor growth to form polycrystalline plates of cadmium telluride (CdTe) 6", 8" and 10" in diameter. The resultant material will be evaluated as substrates for mercury-cadmium-telluride (HgCdTe) growth and as an infrared optical material. Late in the program, mercury vapor will be used in an attempt to grow HgCdTe layers on the large area CdTe plates.

Previous workers have grown large plates of CdTe 6" in diameter transporting the vapor using an inert gas. The starting material was pre-compounded. The method to be used in this program was to compound the material and transport the vapor through a filter into the casting chamber for growth in one operation under vacuum. Solid state recrystallization carried out at high temperatures over a long period of time will produce the desired large grain sturcture.

Results reported in the first two quarters demonstrated the initial process concept was impractical. Vapor transport of compounded CdTe in a sealed evacuated system was too unpredicable. High temperatures coupled with the presence of cadmium oxide caused a high percentage of quartz failures. Program goals could not be reached with the original process approach. The decision was reached to convert to a three chamber quartz system in which the cadmium and tellurium vapors entered the plate chamber from separate tubes. A three chamber approach meant the use of a three zone furnace. A new facility had to be constructed in another building.

The new process approach has been tried three times with

6" diameter plates produced two of the three times. In this process, the program goals of reactant purification and distillation through a quartz filter into the plate chamber are met. The resulting plates have the required large grain structures. The process takes less than 48 hours. Present results indicate scale up to larger plates 8-10" diameter weighing 5-10 Kgms is entirely possible.

Next quarter, efforts will be concentrated on improving the quality of the 6" plates. Methods to produce desired nucleation and growth of the melt will be investigated. The addition of a vapor anneal step in the process will be investigated to reduce the formation of precipitants. A report will be issued recommending scale up of the process to larger diameter plates.

I INTRODUCTION

A crucial problem in the volume production of U. S. Government FLIR systems is the availability of mercury-cadmium-telluride (HgCdTe) detector arrays. Certainly fabrication of the arrays is difficult but the major problem is the availability of high quality detector material. The production of bulk HgCdTe alloy is a slow, difficult low yield process. The preferred method to produce detector materials is to grow HgCdTe layers epitaxially on a high quality cadmium telluride (CdTe) substrate. However, the availability of high quality Cd Te is also limited. Part of the reason for the shortage is that the conventional method for preparing CdTe crystals is to slowly (0.1"/hour) zone refine small diameter (1") crystals using the Stockbarger technique. The purpose of this program will be to develop an alternative approach.

Large plates of high purity large grain cadmium telluride will be grown from the vapor in a sealed sy tem. Cadmium telluride will be compounded from the elements and sublimed through a filter into a separate growth chamber 6", 8" or 10" in diameter. Grain size will be increased by solid state recrystallization. Material thus produced will be evaluated regarding purity, optical homogeneity and suitability as substrates for HgCdTe growth. Attempts will be made to grow HgCdTe layers by mercury vapor deposited on large area plates insitu.

II. VAPOR GROWTH OF CADMIUM TELLURIDE

A. General

Cadmium telluride is formed from the group II element

cadmium and the group VI element tellurium. All II-VI compounds, as they are called, are difficult to grow because of their high melting points and the fact that both constituent elements are volatile. An appreciable vapor pressure exists for each element at the solid melting point which leads to complications for melt growth. For the same reason, vapor growth of the solid becomes attractive.

Solid CdTe may be grown from the vapor at temperatures considerably below its melting point, 1097° C, according to the following equation:

Cd (g) +
$$\frac{1}{2}$$
 Te₂(g) \rightleftharpoons CdTe (s)
Where: g signifies gas or vapor
s signifies solid

The reaction as written is reversible which indicates that solid CdTe will sublime or vaporize into its constituent elements. Thus, the source of Cd or ${\sf Te}_2$ gas may be either the pure heated elements or a heated source of pre-compounded CdTe solid.

The quality of the CdTe grown from the vapor (or melt) depends upon maintaining the exact ratio of 1:1 between the cadmium and tellurium atoms. The pressure of cadmium vapor (pCd) and the pressure of tellurium vapor (pTe₂) in equilibrium over solid CdTe at the growth temperature is very critical and a function of temperature. Deviations from stoichiometry will occur if the ratios are not closely controlled. Supplying the vapors from pure elemental sources heated separately and mixed together at the reaction sight is not too accurate. Even the use of inert carrier gasses does not improve the situation to any great extent. Sublimation of precompounded CdTe followed by removal of the vapor to the reaction sight is far more accurate. The compounded material may

be weighed to an accuracy of 0.1% or better. The accuracy of the ratios may be maintained through direct sublimation in a closed system or through use of an inert carrier gas in a flowing system.

One quality criteria not mentioned thus far is crystallinity. In melt growth, crystals of one single grain may be grown provided that a seed is used and growth rates are very slow. Such restrictions are also the prime limitation relative to diameter of the crystal. In vapor growth, crystals are grown on other crystal surfaces of the same or similar structure, or they grow on an amorphous substrate with spontaneous nucleation and growth occuring over the entire surface. The first case may produce single crystals provided that growth conditions are carefully controlled. The latter method may produce large grain material provided high growth temperatures are maintained over long periods of time.

B. Previous Work

The first extensive investigation of the preparation of CdTe was carried out by D. de Nobel $^{(1)}$ of Phillips. The results published in 1959 details the thermodynamic properties, optical, electrical and semiconducting properties of the materials. The liquidus-solidus curve and related pressure-temperature studies have served as the basis for melt growth of CdTe over the years. Discussions related to melt growth will not be repeated here only as they are relative to vapor growth.

L. R. Shiozawa and co workers at Gould (now Cleveland Crystal Laboratories) carried out an extensive investigation

beginning in the late 1960's concerning the vapor growth of II-VI compounds generally $^{(2)}$ and cadmium telluride $^{(3)}$ specifically. Diagrams from their papers will be used to discuss the problems involved in vapor growth of cadmium telluride.

Figure 1 shows the simple binary phase diagram of the Cd-Te system (2). The diagram indicates a single compound is formed, CdTe, which has a congruent melting point of 1092°C. The term "congruent melting point" indicates that except at perfect stoichiometry, below the 1092°C melting point, both Cd rich and Te rich liquids exist in equilibrium with pure CdTe. The point is better illustrated in the diagram (4) shown in figure 2. Only in a vary narrow range of stoichiometric ratios does the pure CdTe and its equilibrium vapor pressure exist. The range is less than one part per hundred thousand or 0.001 percent. Minimum vapor pressure at all temperature exist along this line. Equilibrium vapor pressure would be exactly in the right ratio. However, considering the accuracy required, it is more likely that the solid cadmium telluride would be either Cd rich or Te rich. Vapors above the solid would reflect this fact and be larger than those above exactly stoichiometric material.

The pressure of cadmium at the cadmium rich boundry stability field as a function of temperature (2) is shown in figure 3. The tellurium rich (2) is shown in figure 4. In both diagrams, the data is compared to the pressure for the pure element, P Cd (1) and P Te2 (1). For the low temperature, the measured values are very close to those for the pure liquid or close to those corrected according to RAOULT's Law. RAOULT'S law states the vapor pressure of a component is lowered by its atomic fraction in a liquid mixture:

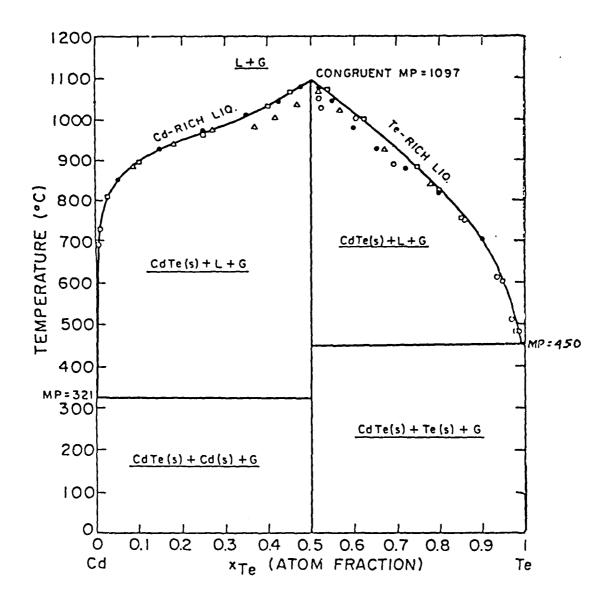


FIG. 1. PHASE DIAGRAM OF THE Cd-Te SYSTEM.

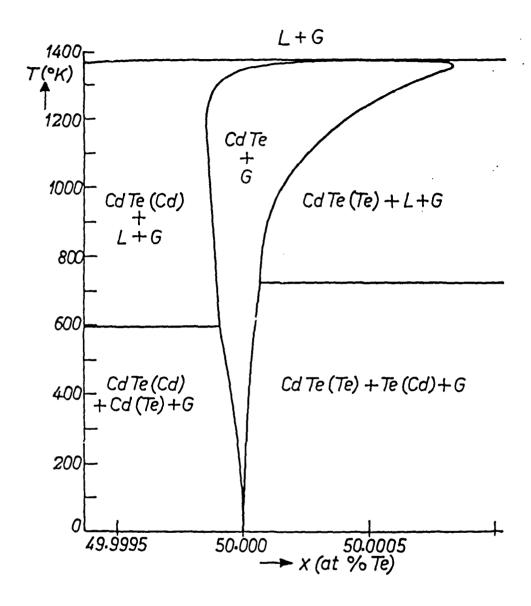


FIG. 2. SOLID STABILITY FIELD OF CdTe.

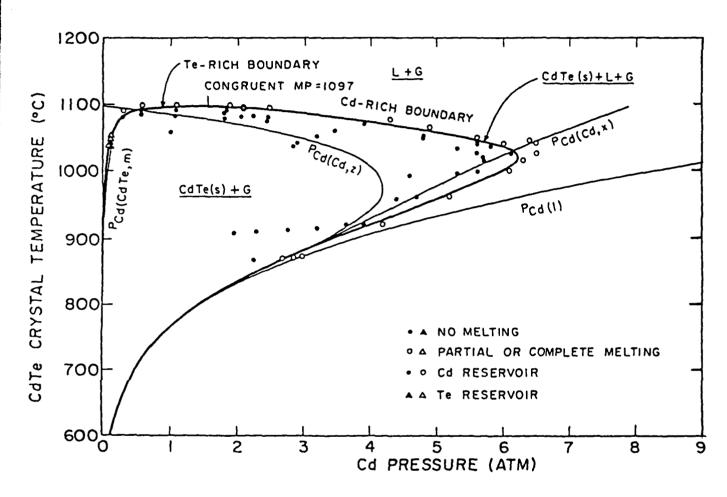


FIG. 3. Cd-RICH BOUNDARY OF THE SOLID CdTe STABILITY FIELD. (PRESSURE-TEMPERATURE PROJECTION.)

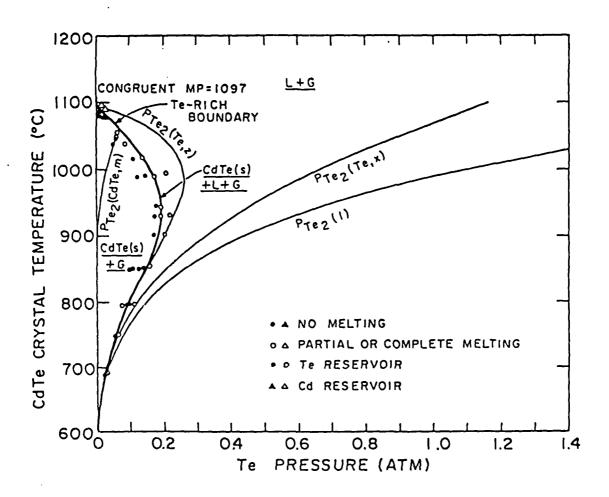


FIG. '4. Te-RICH BOUNDARY OF THE SOLID CdTe STABILITY FIELD. (PRESSURE-TEMPERATURE PROJECTION.)

P Cd = x P Cd (1)

Where $\mbox{\mbox{$P$}}$ Cd is the pressure of cadmium above the melt

P Cd (1) is the pressure of pure cadmium at the temperature of measurement

 ${\sf X}$ is the atomic fraction of cadmium in the melt.

A similar statement may be made for the pressure of tellurium. The calculated curves using X are a simple application of RAOULT'S law. Those using the Z subscript indicates that association between the atoms in the liquid are taken into account. The curves labeled with the M subscript correspond to the minimum pressure conditions which exist with only pure Cd Te solid present.

The diagrams indicate that the pressure of cadmium may become very large, 4-6 atmospheres, around 1000°C when compounding cadmium telluride. The pressure at the congruent melting point, 1092 °C, is about 0.65 atmospheres. The vapor pressure of tellurium is quite low throughout the compounding range. The trick to compounding without an explosion is to stay close to the perfect stoichiometry point and allow time for the liquid phases to become small in quantity. The trick in vapor growth is to be sure that the subliming material is near the stoichiometric ratio so that the resulting vapors are close to the proper ratio. Maintenance of the proper ratio during vapor growth is complicated by the fact that tellurium exists as a diatomic gas, Te2. The effusion rate for a gas is inversly proportional to the square root of its molecular weight and directly proportional to its pressure. Therefore, for CdTe sublimation, we find the effusion ratios to be (2)

 $R \ Cd/R \ Te_2 = (PCd/PTe_2) (MW \ Te_2/MW \ Cd)^{\frac{1}{2}}$ Where R is effusion rate

P is pressure

MW is molecular weight

Even though the vapor starts out at the perfect 2/1 ratio, the cadmium atoms move faster changing the effusing gas mixture ratio. For Cd Te, the ratio becomes 1.33 instead of 2. Build up of the excess component may limit the deposition rate in a sealed system where equilibrium type conditions may be established. The equilibrium constant is given by:

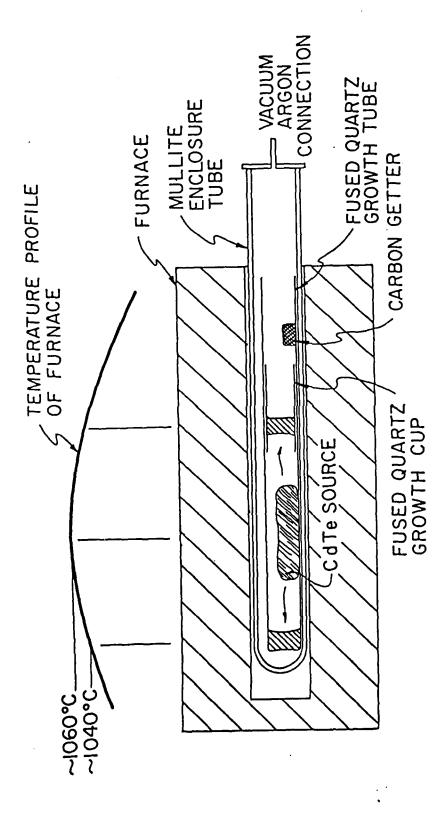
$$K \ Cd \ Te(s) = (PCd) (P \ Te_2)^{\frac{1}{2}}$$

The build up of one component over the other shifts the equilibrium and suppresses further sublimation. Some have used capillary tubes to allow the excess component build up in the vicinity of the source to be pumped away or eliminated. Others have used a carrier gas to carry the subliming vapors, with perfect ratios, to the deposition surface.

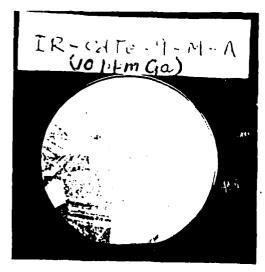
C. Vapor Growth of CdTe Plates

Shiozawa $^{(3)}$ and co-workers at Gould used physical vapor deposition (PVD) to grow CdTe plates up to 6" in diameter. Figure 5 illustrates the type of systems used. Pre-compounded CdTe was sublimed from the hot zone of a furnace to a slightly cooler zone. Best results were obtained when growth temperatures of $1000-1050^{\circ}$ C were used. Recrystallization was allowed to occur over periods up to 400 hours (17 days).

Figure 6 illustrates the type of grain sizes which were obtained. Growth and recrystallization at 950°C produced small grains. Fast deposition and short growth periods even at the high temperatures produced plates with samll grains and voids.

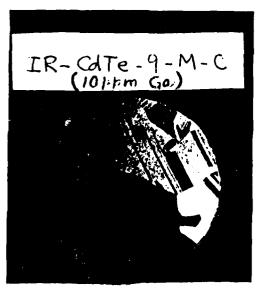


HORIZONTAL SYSTEM FOR CRYSTAL GROWTH BY GRAIN GROWTH . 2



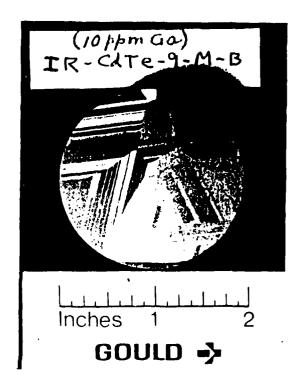
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Inches 1 2

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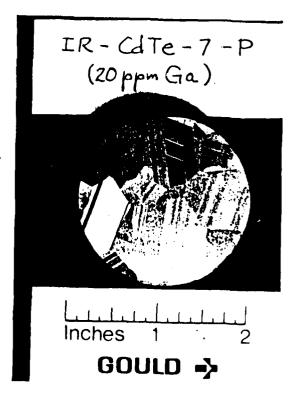


FIG. 6. Lapped Surfaces of CdTe Window Blanks Highlighting Grain and Twin Patterns.

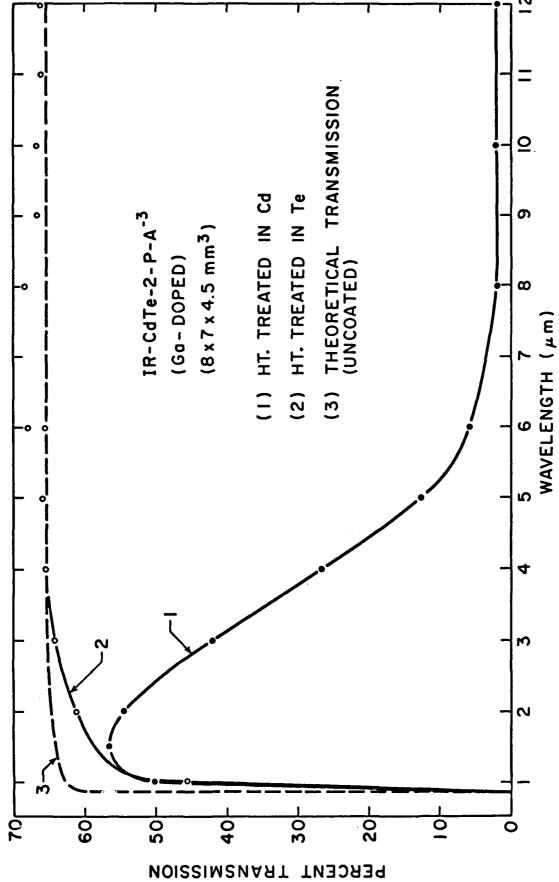
The systems were operated semi-sealed. Argon gas was used as a carrier. Pressures u to 1 atmosphere was used but 180 mm, the vapor pressure of scoichiometric Cd Te at 1050° C, was the preferred pressure. Later versions of the system used graphite parts to minimize the effects of air leaks. Also, inert gas was flowed through the furnace to protect the graphite components.

Plates thus produced were heat treated with both Te_2 and Cd vapors at temperatures of $700\text{-}800^{\circ}\text{C}$. Treatments were alternated and lasted 1-5 days. Measured absorption at $10.6\mu\text{m}$ was $0.001\text{-}0.002~\text{cm}^{-1}$. The effect of heat treating on the infrared transmission of one of their CdTe plates is shown in figure 7. From the transmission for Cd treatment alone, one can see that dual treatment is necessary. After treating with Te_2 vapor, almost theoretical transmission was obtained.

III APPLICATION OF THE AMTIR METHOD TO THE GROWTH OF CdTe

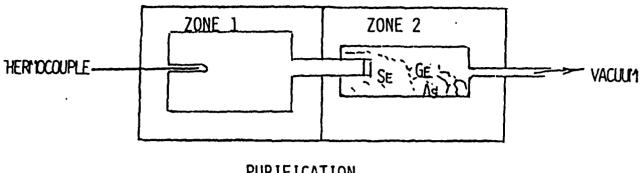
A. Preparation of AMTIR-1 glass

A simplified diagram depicting the glass compounding and casting process developed by Amorphous Materials, Inc. to produce AMTIR-1, is shown in figure 8. A high purity quartz container is placed in a dual zone resistive heated furnace. Zone 1 contains the round empty chamber which will serve later in the process as the casting mold. Zone 2 contains the glass compounding chamber. The process employed at Amorphous Materials combines all three glass processes (element purifications, compounding the glass and casting the plate) into a single continuous process.

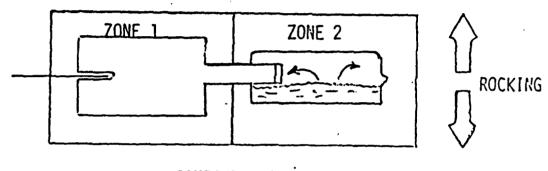


OF Ga-DOPED CdTe OPTICAL TRANSMISSION F1G. 7.

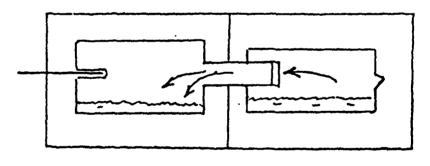
FIGURE 8. GLASS PROCESS DIAGRAM



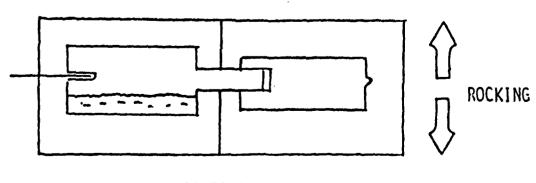
PURIFICATION



COMPOUNDING



DISTILLATION



CASTING

In the first step, both chambers are evacuated and heated to remove moisture. A small amount of aluminum wire is added to the elements to act as a getter of oxides in the molten glass. After several hours, the chamber is sealed off while still under vacuum by heating and collapsing the pumping tube. The furnace is closed and need not be opened again until the glass is quenched.

The temperature is raised in both chambers while rocking the furnace. The casting chamber is heated to prevent premature transfer of the elements from the compounding chamber. The furnace is rocked for several hours to insure that all the elements have reacted properly and are uniformly mixed.

Rocking is stopped and the glass casting chamber cooled to allow transfer of the compounded glass into the casting chamber. Distillation occurs through a porous quartz filter which removes all particulate matter. The distillation generally takes 12-15 hours. The amount of material passed through the frit varies depending upon diameter and thickness. A 6" diameter plate 2" thick requires about 4Kgms of glass while a 8" diameter plate 2" thick requires 7Kgms of material. It is interesting to note that the purity of the finished material improves with quantity prepared. The total amount of impurities from quartz walls, vacuum system, etc. remains constant while the ending concentration decreases with increase in mass. The distilled glass is mixed by rocking. The glass is then allowed to cool while rocking down to the casting temperature range. Rocking is stopped and the furnace leveled up. The glass is rapidly cooled using compressed air to the anneal range 370°C. The glass is annealed 6-8 hours before being allowed to cool to room temperature.

AMTIR-1 glass is compounded in very unique and valuable high purity quartz containers. Casting chambers 6", 8" and 10" in diameter are routinely prepared. Methods have been worked out to open the chambers with a diamond saw so that the cast plate may be removed without breaking. The chambers are cleaned up and resealed for reuse. The compounding tubes are not saved. The impurities within the high purity beginning reactants are left behind during the distillation. The residues are sometimes quite large indicating the effectiveness of the method in preparing high purity solid materials.

B. Modification for Vapor Growth of Cd Te

The temperature range involved in cadmium telluride compounding and solid state recrystallization is $1050\text{-}1100^{\circ}\text{C}$, well above the compounding temperature used for AMTIR-1. However, the furnaces are of sufficient caliber to reach and maintain these temperatures continuously. Times involved are much longer. From start to finish the AMTIR-1 process requires 48 hours to produce a plate. High quality cadmium telluride grown from the vapor with solid state recrystallization (grain growth method) requires 300-400 hours (12-17 days) to produce good quality material 1" thick $^{\circ}$. For a 6" diameter plate, 2700gms of cadmium telluride would be grown. Considering all these factors, the procedure carried out would be as follows:

1. The correct amounts of high purity cadmium and tellurium will be weighed out and placed in the compounding chamber as before. For a 6" plate, about 2700 grams will be required. High purity aluminum wire will be added (10-20ppm) to serve as an oxide getter. The casting chamber may need to be carbon coated using graphite formed from the pyrolysis of acetone.

- 2. The compounding and casting chambers will be heated to 200°C to remove moisture and the chamber will be tipped off.
- 3. The casting chamber will be heated to 1100° C. The compounding side will be heated to the boiling point of cadmium (765°C) and rocking begun. Over a period of hours, the temperature will be increased to 1100° C while rocking to insure complete compounding of the cadmium telluride.
- 4. Rocking will cease and material transfer begun. The casting chamber side will be reduced to a temperature of $1000-1050^{\circ}$ C to bring about transfer of material to the plate side. The high temperature will be maintained so that grain growth will be a continuous process. Particulate matter and oxide impurities will remain behind in the compounding chamber. The time involved may be as long as 10-15 days.
- 5. After completion of the run, the cadmium telluride plate will be removed from the chamber using a horizontal glass saw as is done for AMTIR plates.

C. Program Objectives

A large diameter, thick, high purity, large grain plate of cadmium telluride will be formed. Individual large grains $1\text{-}4\text{cm}^3$ in volume will be visible in the surface of the plate after lapping and light etching. Evaluation and treatment of the plate depends upon the desired use.

First emphasis of the program will be to establish the growth parameters using 6" diameter chambers. Purity of resultant material will be verified by chemical analysis. Electrical, mechanical and optical evaluation techniques will be

used where appropriate. After growth parameters are established, scale up for 8" diameter and 10" diameter plates will occur.

Substrates will be cut out of 6", 8" and 10" diameter plates for evaluation for HgCdTe epitaxial growth. Disks 2" in diameter and 0.1" thick will be prepared for evaluation by groups designated by DARPA.

Disks 2"D x 0.25" thick will be prepared for optical homogeneity verification. The disks will be polished flat and paralled in order to carry out MTF based image spoiling tests. Additionally, lenses will be fabricated for evaluation in the U. S. Army small imager FLIR common Module.

The last goal of the program will be to grow large area HgCdTe layers insitu. Mercury vapor will be admitted into the 6", 8" and 10" diameter CdTe growth chambers in an attempt to produce layer growth of the right composition.

IV. RESULTS FOR THE QUARTER

A. Process Facility

A three zone furnace is too large to fit into our standard AMTIR furnace enclosure. We decided to build a separate facility in our optics fabrication building. A photograph of the enclosure is shown in figure 9A. Not shown in the photograph is a water circulated fan which is used to provide ventilation and to filter the air of noxious vapors when required. The three power units used to control the three zone furnace are shown in figure 9B. The box on the top of the cabinet controls the third zone.

B. Quartz Container

A photograph of the three chamber quartz container is shown in figure 10A. The unit is formed by joining two standard compounding tubes to a 6" plate chamber on opposite sides. The quartz filt_rs are visible in the photograph. The bottom photograph 10B, shows the quartz chambers after they have been loaded with the reactants, cadmium and tellurium, and placed in the three zone furnace. Note the thermocouple placed inside the round 6" plate chamber.

The three zone furnace was constructed by bolting two furnaces together. A standard round chamber furnace was joined to another unit fitted with a clam shell heating element. Both units were bolted to a platform placed on the floor. Because of the change in procedure, a rocking platform was not used. Agitation was not considered necessary. Also, there was reasonable doubt about the ability of a three chamber quartz container to withstand the mechanical strain of agitation.

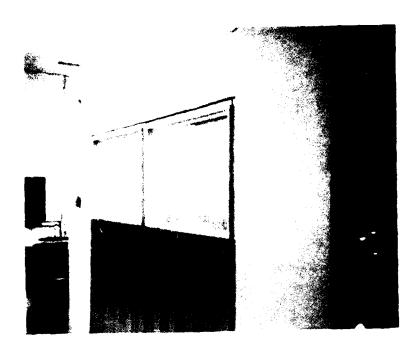


FIGURE 9A Cadmium Telluride Process Enclosure



FIGURE 9B Three Zone Power Controllers



FIGURE 10A Quartz Compounding and Plate Chambers

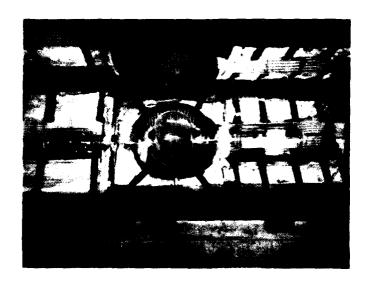


FIGURE 10B Quartz Chambers Containing Reactants
Placed in Three Zone Furnace

C. Plate Results

The procedure followed may be described in general terms. The chambers are evacuated and heated to remove moisture. The temperatures are raised in the two side chambers until the cadmium and tellurium melt. After a period of an hour or more, the pumping tubes are sealed off and the furnace closed. The temperature of the tellurium chamber is raised to 800°C to distill the liquid into the center plate chamber. The distillation for 1Kgm takes about 4 hours. The temperature of the cadmium chamber is raised to 700°C to provide about 0.5 atmosphere pressure. The temperature of the plate chamber and the tellurium chamber are raised steadily towards the 1092°C melting point of cadmium telluride. The melting point was exceeded slightly for a short period of time and then the temperature lowered to the crystal growth temperature of 1080°C. A growth period of only a few hours (four) is required. The furnaces are cut off and allowed to cool to room temperature.

The procedure described is the one now in use. In the first attempt to grow a plate by this method, run #17, the importance of raising the temperature of the empty tellurium chamber as the plate temperature increased was overlooked. As the plate growth temperature of 1000-1100°C was reached, compounded cadmium telluride transferred into the tellurium chamber. Transfer into the cadmium chamber did not occur because of 0.5 atmosphere vapor pressure. As a consequence, the plate produced in run #17 did not weigh quite 1Kgm. The remaining 1Kgm material was deposited as dendrites in the tellurium chamber.

A photograph of the lapped surface of the first plate is shown on figure 11A. Grains over 1" square are visible. The finished plate is about 0.25" thick. Grains reach all the way



FIGURE 11A Photograph of plate from run #17

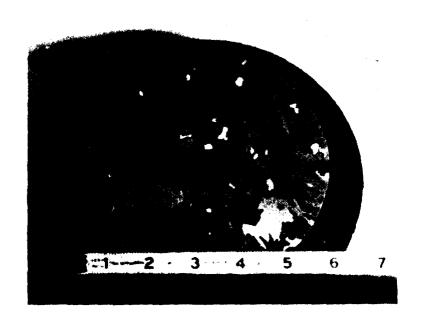


FIGURE 11B Photograph of plate from run #19

through. Twin lines are apparent in some of the grains. After polishing, the plate was examined using an infrared microscope. Some areas of the plate contained precipitants while some were clean. Measured infrared transmission 2.5-25µm showed no evidence of free carrier absorption. High resistivity is indicated. The measured transmission was 53% which compares favorably with the expected absorption free transmission of 65%. The loss in transmission was probably due to poor polish more than absorption by precipitants. Polishing a soft material like cadmium telluride, Knoop hardness of 45, is an art in itself.

The second attempt to prepare a plate was spoiled due to a mistake. Around 1100°C, smoke began to rise from between the two furnaces. The technician mistakenly believed that the quartz container had cracked. The power to the three zones was cut off to prevent further generation of noxious gases. When the furnace was opened several hours later to inspect the damage, the mistake was discovered. Unfortunately, restoring the power settings did not allow recovery of the experiment.

The third attempt was much more successful. A plate weighing over 1Kgm was produced. A photograph of the plate from run #19 is shown in figure 11B. A ruler is shown for reference. Notice the number of large grains is smaller than run #17. Examination revealed that the bottom surface was composed of small grains a few mm's in diameter. We believe the smaller grain structure was the result of our attempt to more closely control the conditions at the point of melting, 1092°C. We controlled the cadmium temperature at 730°C to provide 0.65 atmospheres pressure to produce exactly stoichiometric material at 1092°C. Apparently, we did not wait long enough so that only the top portion melted and formed large crystals.

Grinding and polishing the plate produced results similar

to the previous run. The measured transmission for the plate 0.4" thick was about 25%. Again, the polish quality was poor. Grain boundries were clearly visible on top of the plate. Examination with an infrared microscope indicated more extensive precipitations within the material than run #17. Apparently, higher cadmium pressure will be required to produce better material.

Samples from plate #17 and plate #19 were removed for analysis. The method used will be emission spectrograph carried out by the analytical facility in the Semiconductor Components Group of Texas Instruments.

D. Previous Analysis

Last quarter, samples of cadmium telluride from runs #1, #2 and #7 were submitted to T.I. for analysis. Material from #1 and #2 was CdTe which had been compounded in a tube but did not transfer as a vapor into the plate chamber. Material from run #7 did transfer as a vapor. The analytical results reported are shown on table 1. The first point to notice is that the aluminum used as a getter of oxides is present in the CdTe which did not sublime. The results demonstrate that aluminum is left behind during the vaporization.

The stated purity for the reactants from ASARCO and KBI is 5 9's +. Examination of the results for all 4 samples indicates a purity level of 10-20 ppm if the aluminum and the one spurious Zr value are ignored.

The major impurity in tellurium from KBI and from ASARCO is selenium. The element is not routively detected by emission spectrograph. The other elements Pb, Mg, Si, Fe, Cu, Ag, Na and

TABLE I CdTe ANALYTICAL RESULTS

Element	Sample No. 1 (CdTe #1)	Sample No. 2 (CdTe #2)	Sample No. 3 (CdTe #7 Plate)	Sample No. 4 (CdTe #7 Side)
В	ND	ND	ND	ND
P	ND .	· ND	ND,	ND
Sb	ND	מא	ND	, ND
Ge	ND	ND	ND	ND
Pt	ND	. ND	ND	ND
Au	ND	ND	ND	ND
As	ND	ND	ND	ND
Mn	ND	ND	ND	ND
Pb	D<0.0001	0.0001	D<0.0001	0.0003
Cr	ND	ND	ND	ND
Mg	D<0.0001	D<0.0001	D<0.0001	D<0.0001
Si	D<0.0001	0.0001	D<0.0001	0.0013
Ga	ND .	ND .	ND	ND
Fe	D<0.0001	D<0.0001	D<0.0001	D<0.0001
Ni	ND	ND	ND	· . DD
Bi	ND	ND	ЙD	ND
A1	0.0004	0.0016	ND	ND
Вe	ND	ND	ND	ND
Мо	· ND	ND	מא	ND
Sn	D<0.0001	D<0.0001	D<0.0001	D<0.0001
Ca	ND	ND	ND	ND
v	ND	ND	ND	ND
Cu	D<0.0001	D<0.0001	D<0.0001	D<0.0001
In	ND	ND	· ND	ND
Cd	10-100	10-100	10-100	10-100
٨g	D<0.0001	D<0.0001	D<0.0001	ND
2n	ממ	ND	ND	ND
Ti	ND	ND	ND	. ND
Zr	ND	0.0051	ND	מא.
Pd	ND	ND	DN	סא
Co	ND .	ND	ND	ND
Na	D<0.0001	D<0.0001	D<0.0001	D<0.0001
K	n<0.0001	D<0.0001	n<0.0001	n<0.0001
Li	'' ND	ND	ND	. ND
Te	10-100	10-100	10-100	10-100

Results are in weight percent. D: Detected ND: Not Detected

K are listed as low level trace impurities in the reactants. The results do not demonstrate a purity improvement for the CdTe except that aluminum is removed by distillation.

E. Discussion of Results

Results obtained using the three chamber method indicate that a reliable, fast process to produce large diameter, large grain plates may be developed. The program goals of element purification and distillation through a filter may be realized. Preparation of plates 5-10 Kgms, 8-10" in diameter seems very practical. Considering the preparation may take place in only 48 hours, the process offers an advance in the state of the art. Confirmation of the purity improvement will in the very least provide a rapid, convenient source of precompounded material.

V. Plans for Next Quarter

- 1. Prepare 4 6" diameter plates evaluating (a) crystal growth from the center of the plate (b) heat treating with cadmium vapor as a final step in the process (c) growing plates with larger mass.
- 2. Prepare a report recommending going on to the $8\ensuremath{\text{"}}$ diameter plates.
 - 3. Grow 8" diameter plates weighing 5-10 Kgms.
 - 4. Develop techniques for preparing evaluation samples.

RECERENCES

- "Phase Equilibria and Semiconducting Properties of Cadmium Telluride" By: D. De Nobel Phillips Research Reports 14 361-399 (1959)
- 2. "Research on Improved II-VI Crystals" By: L. R. Shiozawa and J. M. Jost. Clevite Corporation, Cleveland, Ohio Contract No. F33615-68-C-1601_P002 January 1971.
- 3. "The Application of Physical Vapor Deposition to Semiconductor Materials for Use as High Power Infrared Windows" By: L. R. Shiozowa, J. M. Jost and D. A. Robert. Could Laboratories, Cleveland, Ohio Contract No. F33615-71-C-1777 September 1973.

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